

SUM-FREQUENCY SPECTROSCOPIC STUDIES OF MINERAL–WATER INTERFACES

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RESEARCH OBJECTIVES

Interactions of water and aqueous solutions with mineral surfaces play an important role in a variety of environmental processes. These processes include soil formation, cycling of chemical elements in nature, mobility of heavy metals and other contaminants as well as nutrients, and surface growth of microorganisms (Brown et al., 1999). Such interactions are affected by solution pH, the presence of dissolved ions, and the surface structure of the solid. The objective of this project is to use available experimental techniques and theoretical approaches to develop a comprehensive microscopic picture of how water and solutes interact with mineral surfaces.

APPROACH

To study the structure of water at a mineral surface, we use sum-frequency vibrational spectroscopy—a surface-specific technique with monolayer sensitivity that can be applied under ambient conditions (Shen, 1989). The technique is based on sum-frequency generation (SFG), a second-order nonlinear optical process in which two intense input laser beams focused on the medium produce an output beam at the frequency $\omega = \omega_1 + \omega_2$. The process is electric-dipole allowed only in noncentrosymmetric media, and thus it is capable of probing the molecular ordering at the interface caused by the breaking of centrosymmetry at the surface. One of the input beam frequencies is tunable in the range of system vibrational resonances (e.g., water molecule vibrations or metal-oxygen stretching vibrations). Hence, spectroscopic information is obtained from the water layer just at the surface, from which the orientational distribution and structural type of molecular species can be extracted.

ACCOMPLISHMENTS

In the past, SFG has been used to observe ice-like ordering of water molecules on a vitreous silica surface (Du et al., 1994). Here, for the first time we implement sum-frequency vibrational spectroscopy to extend the study to the interface of liquid water and a well-characterized surface (0001) of crystalline quartz (α -SiO₂)—one of the most abundant minerals. We have developed an experimental technique to differentiate a weak SFG signal from a strong background SFG generated in the bulk of quartz crystal (a well-known nonlinear crystal) by use of special experiment geometry and light polarization combinations. Sets of interface water vibrational spectra as a function of pH have been obtained (Figure 1). Comparison with the case of vitreous silica shows that the crystallinity of the surface results in a higher degree of ordering in the interfacial layers of water at a given pH. This is shown by a pronounced red-shifting of the peak associated with the symmetrically (ice-like) coordinated species in the hydrogen bond network of water. With increasing pH, this peak also increases in intensity in both series, reflecting increasing surface negative charge. The data suggest that differing crystallographic surfaces may induce specific variations in water structure in the first few layers, as well as modification of response to pH and sorbing species.

SIGNIFICANCE OF FINDINGS

The measurements provide important information on the microscopic behavior of water in contact with the surface of α -quartz under ambient conditions, and suggest that water on specific mineral surfaces may differ in structural details. This could in part explain the variations of reaction rates on particular mineral surfaces. The study also provides additional constraints for potentials used in molecular-dynamic simulations of water on mineral surfaces, and has allowed enhanced interpretation of sum-frequency spectral features.

RELATED PUBLICATIONS

- Brown, G.E., et al., Metal oxide surfaces and their interactions with aqueous solutions and microbial organisms. *Chem. Rev.*, 99(1), 77–174, 1999.
- Shen, Y.R., Surface-properties probed by 2nd-harmonic and sum-frequency generation. *Nature*, 337, 519–525, 1989.
- Du, Q., et al., Vibrational-spectra of water-molecules at quartz water interfaces. *Phys. Rev. Lett.* 72(2), 238–241, 1994.

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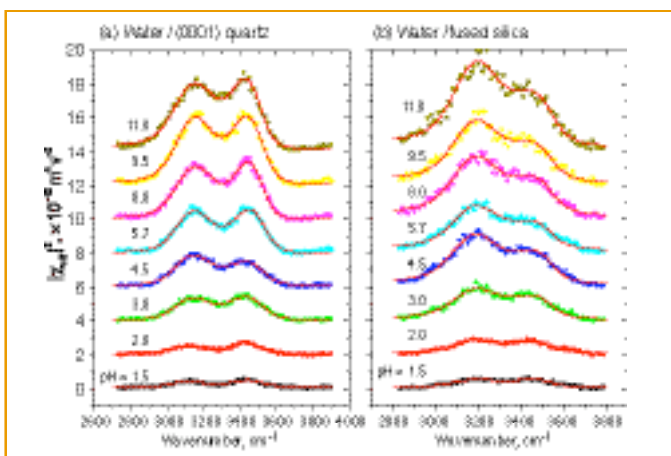


Figure 1. Sum frequency vibrational spectra for water on (a) (0001) α quartz surface and (b) vitreous silica surface as a function of pH. The lower energy peak is due to ice-like structure water, while the higher energy peak is due to water forming several hydrogen bonds.